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Gordon A. Gallup

University of Nebraska-Lincoln, ggallup1@unl.edu

Paul Burrow

University of Nebraska-Lincoln, pburrow1@unl.edu

Ilya I. Fabrikant

University of Nebraska-Lincoln, ifabrikant@unl.edu

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Reply to “Comment on ‘Electron-induced bond breaking at low energies in HCOOH and glycine: The role of very short-lived σ^* anion states’ ”

Gordon A. Gallup, Paul D. Burrow, and Ilya I. Fabrikant

Department of Physics and Astronomy, University of Nebraska, Lincoln, Nebraska 68588-0111, USA

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Rescigno *et al.* [Phys. Rev. A **80**, 046701 (2009)] criticized our theoretical treatment of dissociative electron attachment in formic acid in which we show that this process can be explained by electron attachment into the temporary negative ion state formed by occupation of the $\sigma^*(\text{OH})$ orbital. We argue that their objections do not hold up to scrutiny.

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At issue is whether the dissociative electron attachment (DEA) process in formic acid (HCOOH) and glycine ($\text{NH}_2\text{CH}_2\text{-COOH}$) occurs directly through temporary occupation of the O-H antibonding orbital, similar to HF and other hydrogen halides, or whether it requires the involvement of a $\pi^*\text{-}\sigma^*$ symmetry-breaking mechanism, similar to that required in vinyl- or phenyl-chloride.

Rescigno *et al.* [1] criticized our theoretical treatment [2] of DEA in formic acid and glycine, in which we showed that the DEA cross sections and their fine structure can be accounted for by electron attachment into the temporary negative ion states formed by occupation of the $\sigma^*(\text{OH})$ orbital. This treatment was counter to that for HCOOH proposed by Rescigno *et al.* [3] who argued for electron attachment into the $\pi^*(\text{C=O})$ orbital, followed by out-of-plane motion of the H atom attached to the carbon atom thus leading to coupling of the π^* and σ^* orbitals and then to loss of the H atom from the OH group and production of HCOO^- . Their fixed-nuclei study was based on potential surfaces along a proposed reaction coordinate, but did not include a calculation of the DEA cross section. While the preferred way to resolve this issue would be for them to prove their approach by calculating the cross section, we accept their statement that such dynamical calculations are at present infeasible. We do not claim that such a mechanism could not take place but, rather, that it does not account for the major contribution to the cross section or its sharp structure.

Rescigno *et al.* [1] provided no discussion of DEA in glycine in their comment. However, they suggest that DEA measurements in DCOOH could resolve the controversy since the greater mass of D relative to H would reduce the rate of “required out-of-plane motion.” It appears to us that if this were the case then the cross section of glycine would be greatly reduced by the necessity to move the much larger mass attached to the central carbon atom out of plane. This is contrary to experiment.

Rescigno *et al.* [1] presented two experimental counter arguments to our studies. The first involves collisions between fast K atoms and acetic acid molecules in which electron transfer takes place to produce K^+ and CH_3COO^- [4]. In this work, Brooks suggests that electrons “most likely transfer” into the π^* orbital rather than to a σ^* orbital. Even if this were true, it would be irrelevant because of the substantial differences between free-electron attachment and a heavy particle collision involving much longer interaction times

and perturbations caused by K and the final K^+ product. In fact, Brooks says that “in the present experiment this (symmetry-breaking) deformation is easily provided by the K donor atom.” While we cannot claim expertise in this area, the argument given by Brooks for transfer into π^* seems to rely on the lack of similarity in acetic acid between the shape of the “steric asymmetry parameter” with energy and that observed for transfer to the σ^* orbital of t-butyl bromide. We note that the characteristics of the $\sigma^*(\text{C-Br})$ orbital and the $\sigma^*(\text{OH})$ orbital in acetic acid or HCOOH, however, differ substantially in terms of energy, nodal structure, and charge distribution, and reaching this conclusion in the absence of transfer data in OH-bearing compounds is premature. As noted above, though, heavy particle electron transfer processes do not provide an appropriate model for free-electron attachment.

Their second argument involves a “close” inspection of structure appearing in the HCOO^- yield curve of Pelc *et al.* [5], which we explained in our study. Their claim is that the structure is not correlated with the OH vibrational levels, but in the case of $\nu=4$, the “marked change in slope of the cross section” occurs at 1.55 eV rather than at the vibrational threshold at 1.63 eV, a difference of 80 meV. This argument is not convincing since the energy resolution is no better than 60 meV, and we note that Pelc *et al.* assigned the onset for the DEA process only to within ± 100 meV. This difference certainly falls within experimental uncertainty. Rescigno *et al.* did not comment on the nature of this structure, nor how it would arise from their $\pi^*\text{-}\sigma^*$ coupling model.

With regard to the “weak but definite oscillatory structure which starts near 1.7 eV and extends to higher energies” observed by Pelc *et al.* in the DEA cross sections, these features were not present in our calculations. They may well arise from $\pi^*\text{-}\sigma^*$ coupling; however, they represent only a very small contribution to the total cross section.

Rescigno *et al.* used considerable space discussing other molecules in which $\pi^*\text{-}\sigma^*$ coupling is known to occur. These are well known and we have no points of disagreement with them. Indeed, one of us (P.D.B.) pointed out this mechanism in chloroethylenes [6] and chlorobenzene [7] years ago. Citation of May *et al.* [8] on $\pi^*\text{-}\sigma^*$ coupling in chlorobenzene and acetylene does not add credibility to the analysis of HCOOH. The key element of the discussion of Rescigno *et al.* [1] and their earlier PRL [3] is that out-of-plane motion of the H atom attached to the carbon atom in HCOOH couples

the $\pi^*(\text{C}=\text{O})$ resonance to a σ^* resonance and thereby leads to the HCOO^- product. We have no issue with coupling of π^* to the $\sigma^*(\text{C}-\text{H})$ orbital because it is clearly shown to occur in the experimental data of Allan [9] in the C-H vibrational excitation cross section. As we have pointed out earlier, however, there is no π^* peak in Allan's cross section for excitation of the OH stretch. Moreover, Allan [9] emphasizes several times that "this (O-H) excitation is not due to the π^* resonance" (p. 2943) and "the general shape of the present O-H stretch cross sections and the fact that they are excited even in higher overtones resemble the results in hydrogen halides" (p. 2945). This interpretation is consistent with small coupling of π^* to the OH stretching motion, and by extension, to the $\sigma^*(\text{OH})$ orbital. Quantum chemical arguments can be given supporting this point in terms of the absence of significant change in hybridization of the O atom on the OH group when the H atom on that group moves out of plane.

The "theoretical" counter arguments of Rescigno *et al.* are simply off the mark. First, they claim that "all these (resonance) models have semiempirical parameters." In fact all recent DEA calculations for hydrogen halides and the calculation for formic acid were done *ab initio*. They do contain fit parameters (like the position of the R -matrix pole and the R -matrix surface amplitude), but these are fitted to *ab initio* scattering phase shifts.

Second, Rescigno *et al.* said that our R -matrix parameters "do not take explicit account of target dipole effects" and that our resonance potential curve "is inconsistent with the behavior characteristic of a strongly polar target." This is not the case. Our paper presents the variation in the R -matrix pole, which is equivalent to the diabatic potential curve, and not the adiabatic curve to which they seem to be referring. All dipole effects are included, of course, in our theory by

incorporating the long-range (dipolar and polarization) interaction between the electron and the molecule in the outer region.

Rescigno *et al.* devoted discussion to aspects of treatments of HF by quoting the paper of Morgan and Burke [10] of 1988. It appears that they are not aware of updated *ab initio* results for DEA to HF [11,12]. These results not only confirm earlier "semiempirical" calculations [13], but provide in addition vibrational excitation cross sections, which are in excellent agreement with Allan's measurements [12]. The fact that the scattering phase shift in this system decreases monotonically does not mean that the σ^* resonance does not exist; this simply means that it is so wide that the increase in the resonance phase shift is offset by the background contribution due to the dipole scattering.

More recent calculations on HF also relate to the virtual-state pole problem mentioned by Rescigno *et al.* [1], showing that in the fixed-nuclei approximation a very weakly bound state of HF^- exists. When rotational motion is included the bound state turns into a series of virtual states [14]. Moreover, combined experimental and theoretical investigations allowed establishing the position of these states in the complex k plane [14,15]. The fact that Morgan and Burke [10] did not find the virtual-state poles in their calculations is completely irrelevant to the present discussion. The existence of the virtual states in HF and similar systems is a very well-established fact, and this is what creates cusps in DEA and vibrational excitation cross sections in many systems studied experimentally and theoretically [16].

To sum up, we believe none of the experimental or theoretical criticisms of Rescigno are valid.

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